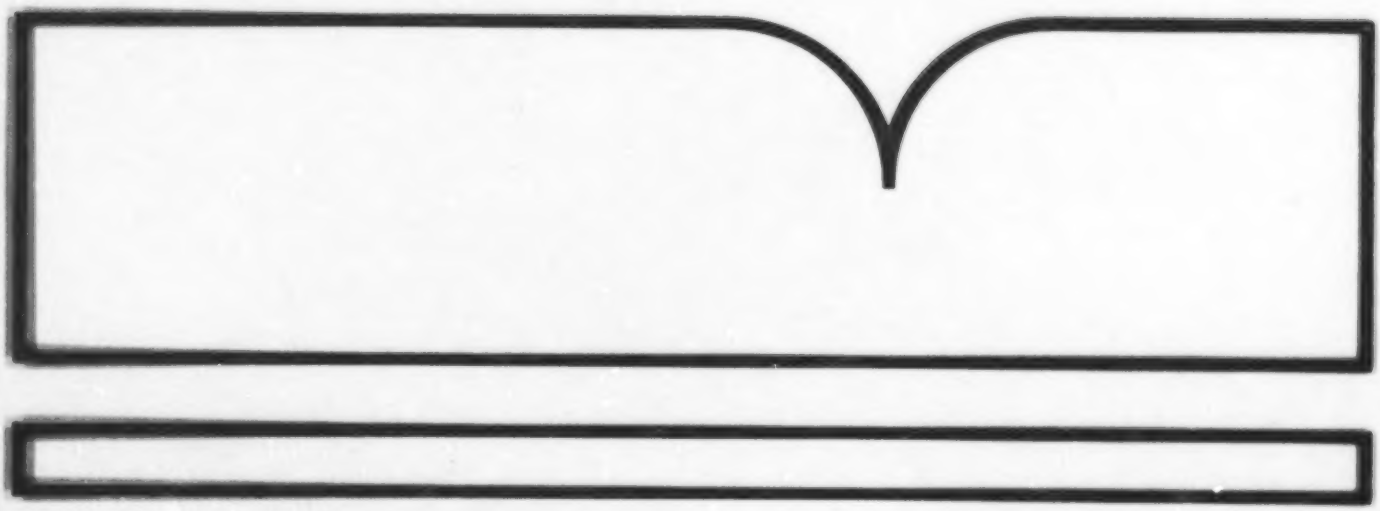
PB85-244234

Summer Internal Phosphorus Supplies in Shagawa Lake, Minnesota

(U.S.) Corvallis Environmental Research Lab., OR

1981



U.S. Department of Commerce
National Technical Information Service
NTIS

TECHNICAL REPORT DATA
(Please read Instructions on the reverse before completir

1. REPORT NO.	2.	3. R PB85-244234
EPA/600/J-81/400		

4. TITLE AND SUBTITLE	5. REPORT DATE
Summer Internal Phosphorus Supplies in Shagawa Lake, Minnesota (Journal Version)	1981
	6. PERFORMING ORGANIZATION CODE
7. AUTHOR(S)	8. PERFORMING ORGANIZATION REPORT NO.
David P. Larsen, Donald W. Schults, and Kenneth W. Malueg	
9. PERFORMING ORGANIZATION NAME AND ADDRESS	10. PROGRAM ELEMENT NO.
Environmental Research Laboratory Office of Research and Development U.S. Environmental Protection Agency Corvallis, Oregon 97333	11. CONTRACT/GRANT NO.
12. SPONSORING AGENCY NAME AND ADDRESS	13. TYPE OF REPORT AND PERIOD COVERED
same	14. SPONSORING AGENCY CODE EPA/600/02

15. SUPPLEMENTARY NOTES

Published in Limnology and Oceanography 26(4): 1981, 740-753

16. ABSTRACT

Phosphorus budget calculations for Shagawa Lake show that significant increases in lake P during July and August 1971-1975 originated from within the lake basin. Mass increases of 2,000-2,900 kg (35-50 ug/liter) were measured, corresponding to internal supply rates of 240-680 kg/wk over a 3-9 week interval. After anaerobic conditions developed in late June, release from the profundal zone sediments contributed significant amounts of P to lake water. Sediment chemical properties were determined to estimate the size of the P reservoir in the profundal zone (at water depths > 6.5m). The P content of the surficial profundal zone sediments was 0.2-0.5% (dry wt) and a significant fraction was potentially mobile (NaoH extractable). We calculate that the upper 10 cm of these sediments contain 50,000 kg of potentially mobile P, of which a small fraction is released each summer. Although external sources of phosphorus have been reduced by about 80% the feedback of P from the sediments is supporting the productivity of Shagawa Lake and may continue to do so for many years.

17. KEY WORDS AND DOCUMENT ANALYSIS

a. DESCRIPTORS	b. IDENTIFIERS/OPEN ENDED TERMS	c. COSATI Field/Group

REPRODUCED BY
NATIONAL TECHNICAL
INFORMATION SERVICE
U.S. DEPARTMENT OF COMMERCE
SPRINGFIELD, VA. 22161

18. DISTRIBUTION STATEMENT	19. SECURITY CLASS *(This Report)*	21. NO. OF PAGES
Release to public	Unclassified	15
	20. SECURITY CLASS *(This page)*	22. PRICE
	Unclassified	

EPA Form 2220-1 (9-73)

EPA/600/J-81/400
JOURNAL ARTICLE

Limnol. Oceanogr., 26(4), 1981, 740–753

Summer internal phosphorus supplies in Shagawa Lake, Minnesota

David P. Larsen, Donald W. Schults, and Kenneth W. Malueg
Corvallis Environmental Research Laboratory, Office of Research and Development,
U.S. Environmental Protection Agency, Corvallis, Oregon 97330

Abstract

Phosphorus budget calculations for Shagawa Lake show that significant increases in lake P during July and August 1971–1975 originated from within the lake basin. Mass increases of 2,000–2,900 kg (35–50 $\mu g \cdot liter^{-1}$) were measured, corresponding to internal supply rates of 240–680 $kg \cdot wk^{-1}$ over a 3–9-week interval. After anaerobic conditions developed in late June, release from the profundal zone sediments contributed significant amounts of P to lake water.

Sediment chemical properties were determined to estimate the size of the P reservoir in the profundal zone (at water depths > 6.5 m). The P content of the surficial profundal zone sediments was 0.2–0.5% (dry wt) and a significant fraction was potentially mobile (NaOH extractable). We calculate that the upper 10 cm of these sediments contain 50,000 kg of potentially mobile P, of which a small fraction is released each summer. Although external sources of phosphorus have been reduced by about 80%, the feedback of P from the sediments is supporting the productivity of Shagawa Lake and may continue to do so for many years.

Lake sediments typically are long term sinks for phosphorus, sometimes retaining 90% or more of the annual incoming P, although 20–50% retention is more common (Vollenweider 1976*a*; Chapra 1975; Larsen and Mercier 1976a; Kirchner and Dillon 1975; Sonzogni et al. 1976). However, over brief intervals, sediments can release significant amounts of P, particularly when overlain by anaerobic or nearly anaerobic water. Slower release can occur under certain poorly identified aerobic conditions (Holdren and Armstrong 1980; Lee et al. 1977). The impact of the internal P source depends on many factors, including the rate and quantity of release and the volume of the water.

Shagawa Lake has provided a case history of a lake's response to reduced P inputs and of sediment-released P which stimulates increased phytoplankton primary productivity and standing crop during summer thermal stratification (e.g. Megard and Smith 1974). Shagawa is a small, shallow, soft-water glacial lake lying in a rock-scoured basin in a boreal forest region of northeast Minnesota (A_0 = 9.5 km^2, $\bar{z}$ = 5.6 m, alkalinity as $CaCO_3$ = 20–25 $mg \cdot liter^{-1}$, specific conductance, 25°C = 65 $\mu mhos \cdot cm^{-1}$). Municipal wastewater from the iron-mining town of Ely (present population, 5,000) has discharged into the lake since the late 1800s. In 1973 a tertiary wastewater treatment plant, built to remove essentially all (≈ 99%) of the sewage P flux to the lake, reduced the annual total P (TP) loading from all external sources by 80% (Sheehy and Evans 1976; Larsen et al. 1975; Malueg et al. 1975). Without an internal supply of P the lake would have been expected to reach a new steady state, with mean P concentrations of 12–14 $\mu g \cdot liter^{-1}$, within 18 months after tertiary treatment began (Larsen et al. 1979). However, 5 years later (1977–1978) winter concentrations were about 20 $\mu g \cdot liter^{-1}$ with average annual values about 30 $\mu g \cdot liter^{-1}$.

Before 1973, average concentrations of TP in the lake showed a characteristic annual cycle, but no other obvious long term trends. Average P concentrations increased during, and especially late in, the ice-covered period. The concentrations declined after ice-out to a mid-June minimum (≈ 20–30 $\mu g \cdot liter^{-1}$) and then increased to an annual maximum in late summer (≈ 90 $\mu g \cdot liter^{-1}$). During fall circulation there was a steady decline to low values before freeze-up. Average concentrations of chlorophyll *a* in the epilimnion also increased during summer from ≈ 10 to 20 $\mu g \cdot liter^{-1}$ to > 60.

We document here the magnitude of

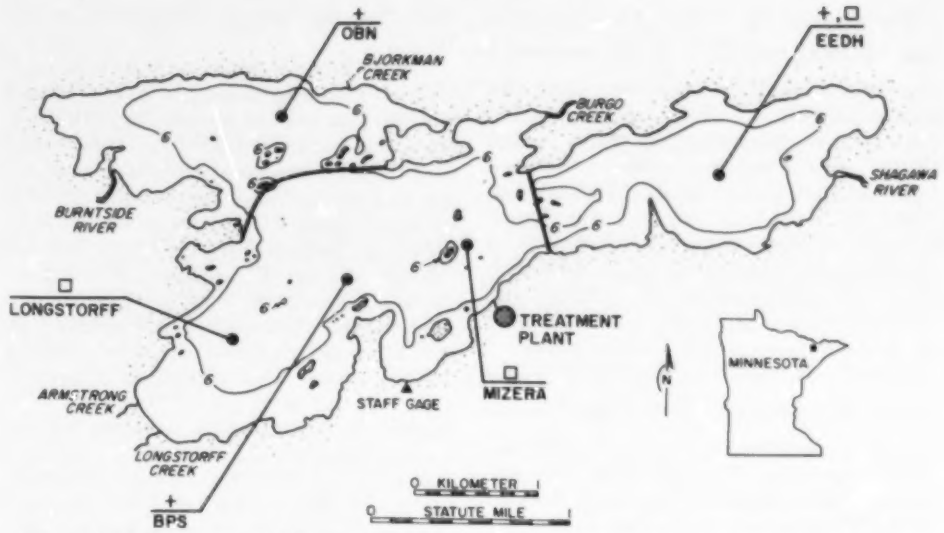


Fig. 1. Bathymetric map of Shagawa Lake showing water sampling stations (+), submerged chamber sites (□), and lake sections used for TP mass calculations.

the summer internal P release during each of 5 years (1971–1975) spanning the onset of tertiary waste treatment and provide evidence that the profundal zone sediments (overlying water depth > 6 m) under anaerobic conditions are the probable source of these seasonal P pulses.

R. Brice, R. Randall, M. Schuldt, and P. Smith were responsible for most of the data collection and chemical analyses. Our results reflect, to a large degree, their efforts. G. Lie, C. Powers, K. Randolph, J. Van Sickle, and R. Stauffer suggested various revisions.

Materials and methods

Shagawa Lake was sampled weekly with a Van Dorn water sampler at three sites at 1.5-m depth intervals from the surface to ≈1 m off the bottom (OBN, BPS, EEDH: Fig. 1). TP was measured by the molybdate method (U.S. EPA 1971) after digestion with persulfate and sulfuric acid, total iron by the phenanthroline method (Am. Public Health Assoc. 1965). Dissolved oxygen (DO) was measured in situ with a Martek Mark II water analyzer calibrated against frequent Winkler titrations (azide modification).

We used the mass balance (input-output) approach advocated by Vollenweider (1976*b*) to account for the fluxes of TP to and from Shagawa Lake, the TP change in the lake, and, by difference, the net fluxes to or from the sediments:

$$\frac{\Delta TP}{\Delta t} = J - Q_o[TP_o] - (S - IS) \qquad (1)$$

where TP (kg) is the mass of TP in the lake; Δt is 1 week; J (kg·wk^{-1}) is the external supply rate; Q_o (m^3·wk^{-1}), the water outflow rate; [TP$_o$] (kg·m^{-3}), the outlet TP concentration; S (kg·wk^{-1}), the sedimentation rate; and IS (kg·wk^{-1}), the internal supply rate. This model is a mass accountability statement for TP: hence an equality should occur if the measurements are accurate. J, Q_o[TP$_o$], and ΔTP/Δt can be measured reasonably well for many lakes, but it is difficult to obtain direct measures for S and IS. Therefore the internal source − sink (S − IS) term is usually expressed as a net flux to or from the sediments and is calculated by difference.

The mass of TP in the lake at any time was calculated as: $TP = \sum_{i=1}^{n} C_i V_i$ where C_i was the concentration representing a volume increment V_i. The lake was divided into sections representing three basins (Fig. 1). These sections were established from distinct morphometric features instead of P distribution characteristics. Volume increments for each section representing each sampling depth were calculated from a volume hypsograph developed from bathymetric characteristics of the lake (Larsen and Malueg 1976).

Weekly surface supplies and losses were calculated from $\sum_{i=1}^{n} c_i f_i$ where c_i was the TP concentration in the ith tributary and f_i represents the daily flow. Concentrations were usually measured weekly in the Shagawa and Burntside Rivers, biweekly in the smaller tributaries, and daily in the wastewater effluent (Schults et al. 1976). Staff gauge heights were measured daily and later converted to flows by the U.S. Geological Survey (*see* Malueg et al. 1975). Daily mass estimates were calculated from linearly interpolated concentration values (Treunert et al. 1974); these were added to provide weekly values.

Three chambers submerged at water depths of 7 m (one in midlake: Mizera; one at the west end: Longstorff) and 12.5 m (at the east end of the lake: EEDH) were used to measure in situ P flux from the sediments during summer 1974 and 1975. Sonzogni et al. (1977) described these chambers and the 1974 results; we include a summary of the 1975 results.

We measured P characteristics of profundal zone sediments to estimate the reservoir of P that could be interacting with overlying waters. The size of this reservoir is critical to the long term recovery of the lake. On six dates (at about 3-month intervals) between 14 May 1973 and 13 September 1974, Ekman dredge samples were taken from 17 stations at water depths ≥ 6 m. The actual sediment depth sampled was difficult to estimate for the relatively unconsolidated bottom, but based on diver observations we believe that the samples represent the top 10 cm.

The sediments were analyzed for total carbon (TC), total nitrogen (TN), TP, and total iron as well as several P fractions. A Hewlett-Packard CHN analyzer was used to measure total carbon and nitrogen in finely ground samples sent to Corvallis, Oregon. TP was measured by acid digestion followed by measurement for soluble reactive P. Inorganic P fractions were measured on samples from seven sites by the methods of Williams et al. (1971*a*,*b*) as modified by R. F. Harris (pers. comm.). The extraction sequence was: 0.1 N NaOH/1.0 M NaCl for 17 h (NaOH-P); 0.22 M sodium citrate, 0.11 M sodium bicarbonate, and 0.5 g sodium dithionate at 85°C for 20 min (CDB-P), and 0.5 N HCl for 1 h (HCl-P). The sum of these measurements approximates, but is probably less than, the total inorganic P component of the sediments (Bannerman et al. 1974; Williams et al. 1971*a*,*b*).

Results

Lake TP changes—Each summer in 1971–1975 the TP content of Shagawa Lake increased 2.5–3.5-fold over a 1–2 month period from late June through August (Table 1 and Fig. 2). TP_{min} values of 1,410–1,890 kg during late June and early July rose to TP_{max} of 4,310–4,770 kg during August in 1971–1973. In 1974 and 1975, TP_{min} (980–1,110 kg) and TP_{max} (3,140–3,630 kg) during these months were well below those of previous years as the lake responded to phosphorus reduction. TP increased in the lake at a rate of $\approx$320–380 kg·wk^{-1}, except in 1974 when the rate was about twice as high; however, the interval over which P increased was significantly shorter than in the other years (Table 1). This pulse can be characterized by a steady increase through mid-August, followed by slight or negligible change until the onset of fall circulation in late August or early September, when steady deposition began (Fig. 2). During 1974, the rapid increase ended in late July and deposition began immediately. Observed lake increases were 2,650–2,990 kg (TP_{max} –

Table 1. Summary of changes in TP content. Column headings defined in text.

Year	Interval (wk)	TP_{min}*	TP_{max}*	$TP_{max} - TP_{min}$	$\frac{\Delta TP}{\Delta t}$
		(kg)			(kg·wk^{-1})
1971	9 (22 Jun–24 Aug)	1,410	4,310	2,900	320
1972	9 (20 Jun–22 Aug)	1,890	4,770	2,800	320
1973	8 (20 Jun–21 Aug)	1,640	4,310	2,670	330
1974	3 (4 Jul–30 Jul)	1,110	3,140	2,030	680
1975	7 (2 Jul–19 Aug)	980	3,630	2,650	380

* Mean values calculated using values circled in Fig. 2.

TP_{min}) for other years, but during 1974 lake TP increased only 2,030 kg (Table 1). These increases correspond to average increases in lake TP concentration of 35–50 $\mu g \cdot liter^{-1}$ during this period.

We attribute the distinctly different pattern of 1974 to the combined effects of strong winds which aerated the entire lake during 26–29 July (>1.0 $mg \cdot liter^{-1}$ DO) and of early initiation of fall circu-

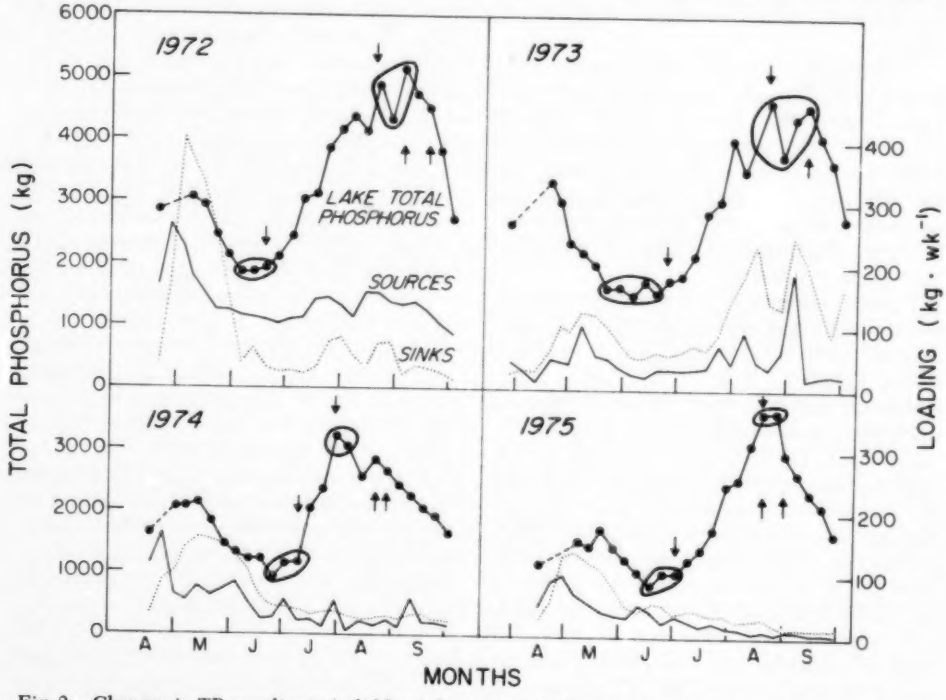


Fig. 2. Changes in TP supplies to (solid line), losses from (dotted line), and mass in (●) Shagawa Lake, April–September. Enclosed dots—those used to obtain TP_{min} and TP_{max} mass values. Downward-pointing arrows delimit time intervals chosen to represent summer pulse. Upward-pointing arrows indicate when fall circulation began and when lake was first well mixed; during 1973 complete circulation occurred within 1 week. Dashed lines—ice break-up (lake was not sampled).

Table 2. TP imports (ΣJ), exports ($\Sigma Q_o[TP_o]$), and estimated internal supply during intervals specified in Table 1.

Year	ΣJ	$\Sigma Q_o[TP_o]$	$\Sigma J - \Sigma Q_o[TP_o]$	Net internal supply	$S - IS$
	(kg)				(kg·wk^{-1})
1971	760	620	140	2,760	310
1972	1,140	390	750	2,130	240
1973	360	840	−480	3,150	400
1974	90	110	−20	2,050	680
1975	130	260	−130	2,780	400

lation. One direct effect of the windstorm was to increase the lake TP content by 840 kg within 1 week. Then deposition began (Fig. 2). Anaerobic conditions were re-established at the greatest depths sampled by 6 August, but there was negligible release of P because the areal extent of oxygen depletion was probably confined to the deeper basins. By 27 August, fall circulation began stimulating P deposition which continued throughout autumn.

There was a similar situation in 1971 when the lake was aerated between 20 and 27 July, with an increase of ≈630 kg TP in 1 week, followed by deposition of ≈760 kg. Anaerobic conditions were re-established by early August and remained until fall circulation in mid-September. During this interval, lake TP increased ≈1,590 kg.

Table 2 summarizes imports to and exports from Shagawa Lake for the June–August interval. Since $TP_{max} - TP_{min}$ (from Table 1) $\gg \Sigma J - \Sigma Q_o[TP_o]$ (from Table 2) for the June–August interval each year, within-lake P sources must be significant. In 1971 and 1972 $\Sigma J - \Sigma Q_o[TP_o]$ accounted for only ≈5 and 26% of the measured change ($TP_{max} - TP_{min}$). During this same interval in 1973–1975, $\Sigma Q_o[TP_o] > \Sigma J$. Thus, net increases in lake P ($S - IS$) ranged from 2,050 kg (1974) to 3,150 (1973), corresponding to net internal supply rates of 240–400 kg·wk^{-1} (680 kg·wk^{-1} in 1974: Table 2).

Deposition rates—The TP input-output approach estimates only net fluxes of P to or from the sediments. We attempted to determine gross fluxes by taking deposition into account. During May–June, TP typically declined from high values in mid-May to minimum values in June (*see Fig. 2*). Loss rates averaged 200 kg·wk^{-1} (range = 140–290) corrected for $J - Q_o[TP_o]$, equivalent to a 1.5%·d^{-1} loss of the particulate P (estimated as TP − soluble reactive P) in the lake. This loss rate is consistent with values reported by Rigler (1973) and Schindler et al. (1973). Rigler's results pertain to the epilimnia of several lakes. Our loss estimates from the upper 5 m of Shagawa Lake and from the entire lake were about equal.

If deposition in Shagawa Lake continued through late June–August at rates similar to those during May and June, we would expect loss rates of 200 kg·wk^{-1}. A slightly higher 240 kg·wk^{-1} is calculated from a 1.5%·d^{-1} loss rate. The average net release rate for the June–August period is ≈350 kg·wk^{-1} (excluding 1974: Table 2). Thus, gross release rates for this period might be about 550–590 kg·wk^{-1}, ≈1.5 times the net release rate.

It is possible that net and gross release rates were similar during June–August and that the above estimates of deposition for the interval are unrealistic. Gross release rates were estimated from P lost during spring, when diatoms dominated the phytoplankton and nutrients (nitrogen and phosphorus) were depleted. Later, blue-greens were the dominant algae. These are often neutrally or positively buoyant, while diatoms tend to settle rapidly, particularly if they are nutrient-deficient. During summer most of the particulate P in Shagawa Lake was associated with algae (U.S. EPA unpubl.). Thus, deposition rates and deposition rate coefficients calculated for spring could overestimate deposition during late summer.

Areal release rates—The inception of

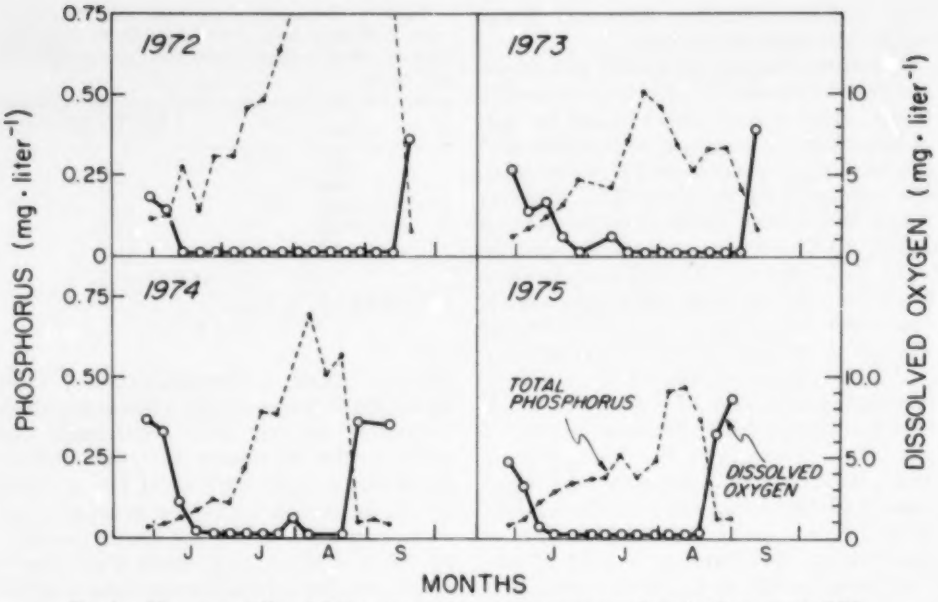


Fig. 3. Changes in TP and DO concentrations at greatest sampling depth at station BPS.

the TP increase, especially near the bottom, corresponded closely to the disappearance of DO in the deeper waters, suggesting that sediments overlain by anaerobic water might be responsible for the lakewide increases. Mortimer (1941–1942) and Syers et al. (1973) reported that the mobility of sediment P increases dramatically when iron-phosphorus complexes dissociate at redox potentials of about +200 mV; a DO concentration ≈1 mg·liter^{-1} might signify this redox potential (Mortimer 1971). In Shagawa Lake's deepest areas, DO concentrations decreased to this level in early to mid-June each year (Fig. 3). TP concentrations began to increase dramatically; in some cases the beginning of this increase seems to have preceded the time at which DO reached 1 mg·liter^{-1}. Increases in total Fe and TP concentration are highly correlated at the greatest sampling depths (Fig. 4). This correlation is consistent with the mechanisms for P release proposed by Mortimer (1941–1942).

The increase of TP in deeper waters does not necessarily imply that P originated from the sediments. Increases can result when settling particulate material accumulates and is mineralized in the denser near-bottom water (Schindler and Lean 1974); however, since lakewide increases in Shagawa Lake cannot be accounted for by net imports, a redistribu-

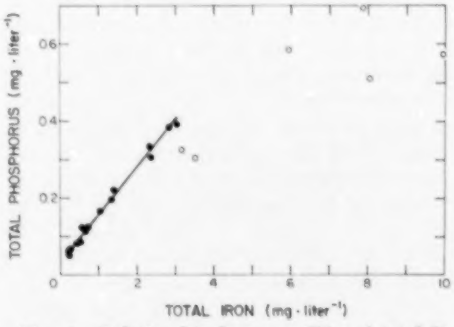


Fig. 4. Relationship between TP and total Fe concentrations in near-bottom water at BPS sampling site, 11 June and 20 August 1974. ●—Samples obtained through 30 July; ○—samples obtained after 30 July. Regression line is (excluding ○): TP (mg·liter^{-1}) = 0.032 + 0.124 Fe (mg·liter^{-1}); r = 0.99.

tion of P causing the measured deep-water increases is unlikely.

If P were released only from sediments overlain by anaerobic or nearly anaerobic water, areal release rates could be calculated from an estimate of that area and the rate of appearance of TP in the lake. We estimated the depth at which DO was 1 $mg \cdot liter^{-1}$ from linear interpolation of weekly DO profiles at two stations in 1971 and three in 1972–1975 and calculated the bottom areas overlain by anaerobic water from these depths. The depths remained relatively stable during July and early August in 1972, 1973, and 1975; but during 1971 and 1974, summer windstorms increased DO concentrations >1 $mg \cdot liter^{-1}$ throughout the lake. During 1972, 1973, and 1975 the estimated mean depths of the 1 $mg \cdot liter^{-1}$ DO isopleth were 7.5, 9.9, and 8.5 m for late June to mid-August. Bottom areas beneath these depths were 2.8, 0.4, and 1.3 km^2. Net areal TP release rates of 12, 161, and 44 $mg \cdot m^{-2} \cdot d^{-1}$ result from the net release rates summarized in Table 2.

These calculations assume that the DO concentrations over the profundal plain are the same as those at corresponding depths above the deep-hole sampling sites. Because the 1 $mg \cdot liter^{-1}$ DO isopleth is shallower above the profundal plain sediments (R. Stauffer pers. comm.), we also calculated release rates assuming that release occurred over the lake's entire profundal zone. Shagawa Lake is characterized by relatively steep sides and a fairly flat bottom with several depressions. The slope changes markedly at about 6.4 m; this depth encompasses an area of about 4.9 km^2—slightly more than half of the surface area. Net release rates estimated to occur from the profundal zone ranged from 7.0–13.1 $mg \cdot m^{-2} \cdot d^{-1}$ (mean = 10.2; Table 3). The values for 1974 are excluded because so much TP appeared in response to high winds. The mean release rate corresponds to an areal release rate of 5.3 $mg \cdot m^{-2} \cdot d^{-1}$ if the entire lake bottom released P equally.

The TP release rates for the submerged chambers for 1974 and 1975 are summarized in Table 4. Sonzogni et al. (1977) described the release characteristics measured during 1974. Although the water in the chambers was still aerobic, there was a slight buildup of TP, at a rate of <1 $mg \cdot m^{-2} \cdot d^{-1}$. Oxygen generally became depleted within 2–3 weeks (weekly samples) after the beginning of an experiment, so that a reliable estimate of aerobic release was difficult. Under anaerobic conditions, the mean release rate was 7.0 $mg \cdot m^{-2} \cdot d^{-1}$ during 1974 (four experiments) and 7.4 during 1975 (three experiments). These could be underestimates because turbulence was lower inside than outside the chambers. Divers who visited the chambers weekly sometimes saw outside movement of sediment floc at speeds up to ≈ 10 $cm \cdot s^{-1}$, which could stimulate a more rapid exchange across the sediment–water interface.

Table 3. Estimates of anaerobic areal TP release from profundal zone sediments. These estimates assume TP is released only from profundal zone sediments.

Year	Net areal release ($mg \cdot m^{-2} \cdot d^{-1}$)
1971	9.0
1972	7.0
1973	13.1
1974	19.8*
1975	11.7
	Mean = 10.2

* 1974 value excluded from mean.

Vertical transport of P—If the profundal zone sediments are the major internal source of P for the lake, then rational mechanisms by which P is transported into the epilimnion must be identified. Stauffer and Lee (1973) showed that significant amounts of P entered the epilimnion of Lake Mendota via entrainment. This process is also important in Shagawa Lake during July and August. Because Shagawa is shallow and because its major axis aligns with the generally prevailing southwesterly winds, entrainment occurs relatively often and transports significant amounts of P into the photic zone during July and August. Figure 5 and Table 5 show several examples of changes in TP in the lake in response to wind-mixing.

Table 4. Anaerobic phosphorus release rates ($mg \cdot m^{-2} \cdot d^{-1}$) measured in submerged chambers.

Location	1974*		1975†	
	Anaerobic interval	Release rate	Anaerobic interval	Release rate
EEDH	5 Jun–31 Jul	7.5	31 Jul–25 Sep	7.5
	8 Aug–27 Sep	6.9		
Longstorff	3 Jul–20 Sep	7.5	17 Jul–25 Sep	8.3
Mizera	18 Jul–15 Aug	6.2	17 Jul–25 Sep	6.3

* Values from Sonzogni et al. 1977.
† Values from D. W. Schults unpubl.

The lake is divided into two zones at the 5-m depth; the upper zone approximates the photic zone and represents ≈70% of the total lake volume. Significant increases in photic zone TP are evident. Although there are also significant decreases in TP in the deeper zone, in no case did the decrease account for the increase in the upper zone. This discrepancy might result from transport from the littoral as Lie (1978) suggested or from an underestimate of the amount of TP in the lower zone.

Eddy diffusion also can transport significant amounts of P upward in Shagawa Lake. Although turbulence is minimal across the thermocline, if there were strong P gradients, significant P transport could take place. Gradients of TP below 5 m in the lake were commonly 50–100 $\mu g \cdot liter^{-1} \cdot m^{-1}$ and often significantly higher near the bottom. If we assume that Fick's first law is applicable and that the vertical diffusivity (K_z) is ≈0.01 $cm^2 \cdot s^{-1}$ (Snodgrass and O'Melia 1975; Imboden and Emerson 1978), vertical flux estimates of 4.5–9 $mg \cdot m^{-2} \cdot d^{-1}$ result. This corresponds to a 150–300 $kg \cdot wk^{-1}$ transport of TP across a plane of the area of the profundal zone. Thus it appears that vertical transport of P via both entrainment and vertical diffusion is significant in Shagawa Lake.

Table 5. Summary of transfer of TP (kg) into the upper 5-m zone, resulting from wind-mixing.

	0–5 m		>5 m	
	Mass	Change	Mass	Change
1971				
20 Jul	2,000		1,100	
27 Jul	2,700	+700	1,030	−70
1972				
1 Aug	1,790		2,360	
8 Aug	2,680	+890	1,720	−640
1974				
23 Jul	990		1,400	
30 Jul	2,230	+1,240	990	−410
1975				
5 Aug	1,500		1,070	
12 Aug	2,380	+880	730	−340

Sediment characteristics—Components of the dried sediments included carbon, 11.2% (SD = 2.6); nitrogen, 1.3% (SD = 0.45); TP, 0.23% (SD = 0.13); and iron, 4.8% (SD = 0.86). These values are overall averages of those in Table 6. The variations in carbon, nitrogen, and iron were unrelated to depth. However, the TP content of sediments at >10 m was nearly three times that at the shallower sites (Table 6). Of the TP at 6- and 7.5-m water depths, 14.4% was HCl-P, 18.8% was CDB-P, and 27.7% NaOH-P; at depths >10 m, 5.2% was HCl-P, 10.0% was CDB-P, and 72.8% was NaOH-P. The sediments at depths >10 m had significantly greater amounts of NaOH-P than did those at the shallower sites. The differences between the NaCl-P and CDB-P contents at the shallow and deep zones were not statistically significant (*t*-test for unequal *n* and unequal variance; $P = 0.05$). The large variation in the TP content was mainly associated with variation in the NaOH-P fraction (TP = 0.1229 + 0.101 NaOH-P; $r = 0.99$).

Discussion

Each year during July and August (1971–1975) the TP content in Shagawa Lake increased significantly. The internal supply of 2,000–3,000 kg over the 1–

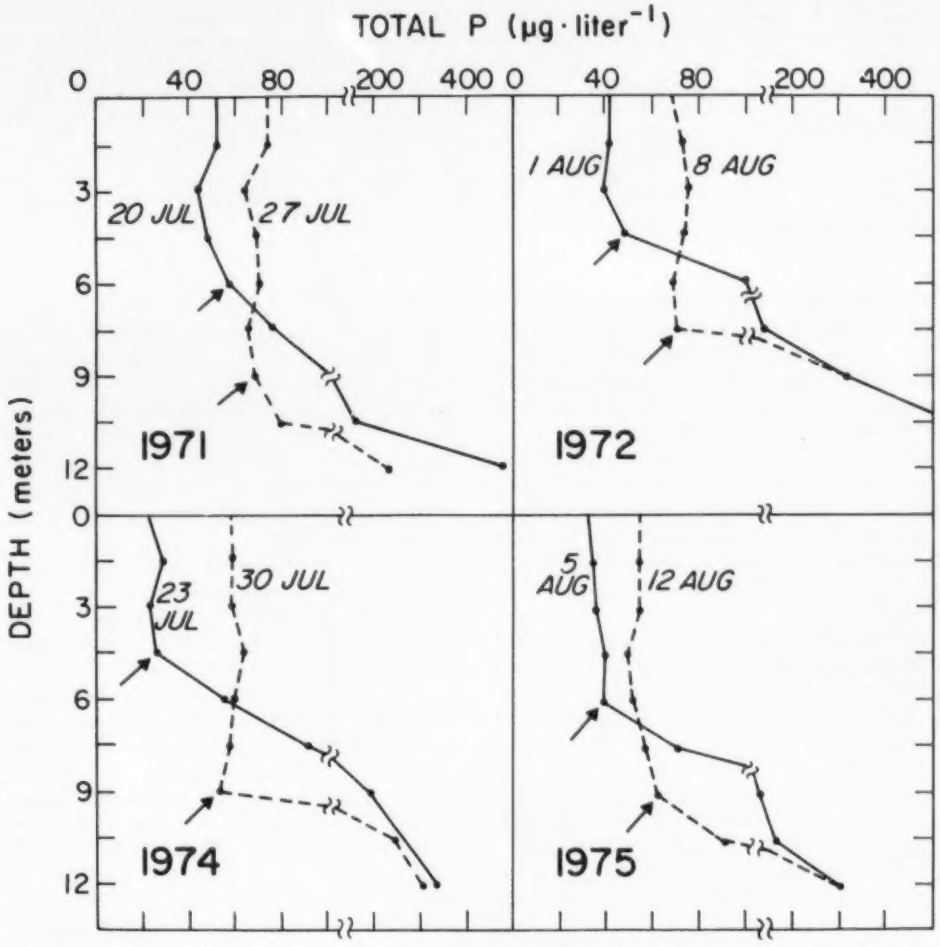


Fig. 5. Changes in TP profiles at BPS sampling site resulting from thermocline erosion. Arrows—approximate depth of mixing.

Table 6. Average chemical characteristics of sediments (% dry wt), 1974 and 1975; $\bar{x}$—sample mean, SD—sample standard deviation; n—number of samples analyzed (n is not constant because not all analyses were made on all samples).

Depth (m)		C	N	P	Fe	HCl-P	CDB-P	NaOH-P
6–10	$\bar{x}$	11.0	1.3	0.18	4.7	0.026	0.034	0.050
	SD	2.7	0.4	0.05	0.85	0.004	0.010	0.010
	n	70	70	82	12	23	23	23
>10	$\bar{x}$	12.3	1.6	0.46	5.0	0.024	0.046	0.335
	SD	1.7	0.2	0.15	0.88	0.020	0.016	0.135
	n	15	15	18	10	18	18	18

2-month interval is about half the annual ≈5,000 kg supply before the removal of P by tertiary wastewater treatment (Malueg et al. 1975) and exceeds the present annual external supply of 1,000–1,500 kg.

Potential sources of TP in the lake are sediments within the mixed and stratified zones. Some sediments within the mixed zone support significant macrophyte growths and some do not. Also, recently settled particulate materials which might not be considered sediments, like algae, could contribute P on dissolution. It is also possible that the P increases could have come from a zone of high P concentration in areas not sampled routinely, such as the near-bottom water.

Of those potential sources of internal P, the profundal zone sediments are certainly significant. The initiation of the pulse measured in the lake corresponds to the onset of anaerobic conditions in the deeper waters. The premise that anaerobic conditions are important for the development of the P pulse in the lake is supported by three other observations. First, lakewide decreases in TP began when fall circulation, aerating the lake, began. If aerobic release were important, particularly when associated with the increased turbulence of fall circulation, further increases would have been expected. Second, a strong windstorm aerated the lake (>1 mg·liter^{-1} DO throughout) in late July 1974. Although TP increased immediately, between 23 and 29 July, probably associated with the direct effects of turbulence, it began to decline shortly thereafter (Fig. 2), well before the onset of fall circulation. Third, aerobic release inside the submerged chambers was minimal. Thus, although others have shown that aerobic release of P from sediments can be important (e.g. Kamp-Nielsen 1974, 1975*a*,*b*; Porcella et al. 1970), we believe that aerobic release did not contribute significantly to the June–August TP pulse in the lake.

The release rates of anaerobic sediments measured or estimated for Shagawa Lake (Tables 3 and 4) generally agree with long term net release rates noted by others. Vollenweider (1968) estimated an average P release of 9.7 mg·m^{-2}·d^{-1} over two anaerobic periods of about 155 days in the Baldeggersee (Switzerland). Welch (1977), using cylinders placed in the bottom of Lake Sammamish (Washington), reported anaerobic release rates of 3–4 mg·m^{-2}·d^{-1}. Burns and Ross (1972) estimated in situ anaerobic release rates of 7.4 mg·m^{-2}·d^{-1} (including hypolimnetic mineralization) for Lake Erie. Sonzogni (1974) calculated 10.8 and 7.2 mg·m^{-2}·d^{-1} for Lake Mendota (Wisconsin), using two different methods, for anaerobic intervals. Cooke et al. (1977) estimated rates ranging from 2.2 to 9.9 mg·m^{-2}·d^{-1} in Twin Lakes (Ohio), if all P was released from sediments overlain by anaerobic water. Ahlgren (1977) reported net phosphorus release from sediments of Lake Norrviken ranging from 2 to 9 mg·m^{-2}·d^{-1} during summer stratification for 1971–1976; the rates declined each year as this lake recovered from wastewater diversion.

Figure 5 and Table 5 show that significant amounts of TP can be transferred into the upper 5 m by entrainment in Shagawa Lake, but the increases in TP in the upper zone were greater than the decreases in the lower zone, implying additional sources. Lie (1978) showed that the littoral zone often has higher TP concentrations than the open water, so that transport toward the open water would be expected; he concluded that the macrophyte communities in the lake contributed a significant amount of P to the pelagic zone during the June–September period in both 1974 and 1975, even though they occupy only a small fraction of the lake bottom area (≈7%). Rapid recycling from detritus deposited after the spring bloom could also provide additional P. Barica (1974) showed that recycling of nutrients from previously sedimented remains of algal blooms stimulated subsequent growth in pothole lakes in southwest Manitoba. We estimate that ≈670–1,220 kg of TP were deposited after the spring maximum in Shagawa Lake, some of which was probably refractory. The amount of refractory P in algal remains and detritus varies from

near zero to >90% (e.g. Golterman 1973; Foree et al. 1971). If all the TP deposited after the spring bloom in the lake were recycled within several months of deposition, this recycling might account for 30–50% of the net amount that appeared during summer. Any fraction of deposited TP that is refractory would reduce the contribution of this source to the summer pulse.

Benthic invertebrates (Gallep et al. 1978) or bottom-feeding fish (Lamarra 1975) may be important in transporting P from sediments to overlying waters. In Shagawa Lake, benthic invertebrate populations typically declined to minimum numbers during late June through July (1,200–1,600 organisms·m^{-2}). However, if invertebrates were important in transporting P, their effect should be greatest when the greatest numbers were found, that is in May–June and September–October (6,000–10,000 organisms·m^{-2}), periods when TP declines significantly in the lake. Fish (mainly *Perca, Percopsis,* and *Catastomus*), whose diet includes benthic invertebrates, reached densities of about 3.5 g·m^{-3}, but were generally about 0.8–1.5 g·m^{-3} in June–August 1974–1976 in waters <5 m in Shagawa Lake (W. A. Swenson pers. comm.). Because most of the fish congregated near the bottom, these numbers also approximate areal densities (m^{-2}). Lamarra (1975: table 5) showed that carp, which are primarily benthophagous, excrete 1–2 mg P·m^{-2}·d^{-1} at densities of 20 g·m^{-2}. If we use these rates for the Shagawa Lake fish populations (even though these fish are not benthophagous), fish would transport <0.1 mg P·m^{-2}·d^{-1} from sediments to overlying water in the lake. Thus it is unlikely that either benthic invertebrates or fish populations play an important role in contributing to the June–August TP pulse.

We do not mean to discount entirely the effects of mechanisms other than anaerobic P release on the dramatic increase in TP in Shagawa Lake during June–August. Certainly all those mechanisms contributed to some extent, particularly if large differences between net and actual gross increase of TP in the lake existed. We estimate that the P-rich sediments of the profundal zone released significant amounts of P when anaerobic conditions developed and that this P was transported into the mixed zone during late June–August, before fall circulation.

Sediment phosphorus characteristics might provide qualitative information about the store of P in the lake bottom and thus about the long term potential for Shagawa Lake's recovery. Wildung and Schmidt (1973) analyzed the upper 10 cm of Shagawa Lake sediments (collected by Ekman dredge) at 31 stations in water depths of 2–12 m. Mean total and inorganic P (% dry wt) were 0.12 (range = 0.09–0.17; SD = 0.02) and 0.07 (no range given; SD = 0.02); organic P, determined by difference, was 0.05 (no range given; SD = 0.02). They found a slight (r = 0.34) but statistically significant (P = 0.05) correlation between TP and water depth. Waddington and Wright (unpubl.) analyzed the top few centimeters of the sediments from 100 sites in Shagawa Lake. TP (% dry wt) ranged from 0.09 to 0.54 (mean = 0.21; SD = 0.09); higher values (0.25–0.54) generally occurred in the deep holes and in some locations on the profundal zone plain. They also took a core in ≈7 m of water near the narrowest section of the lake, where they estimated that only 2.5–3 cm of sediment had accumulated since about 1890 when local logging and mining operations began. Beneath this depth, TP was about 0.1%; above it, about 0.2%. Bradbury and Waddington (1973) took a core beneath 12 m of water at the east end of the lake. They ascribed a sediment depth of 30 cm to the year 1890, based on a sharp increase in hematite grains. Beneath that depth, TP (% dry wt) was relatively constant at slightly <0.1%. It increased to slightly >0.1% at 30 cm and remained generally constant to 14 cm where TP was measured at slightly >0.3%. Another increase began at 10 cm, reached a maximum of about 0.5% at 4 cm, and declined to about 0.3% at the surface.

The values of surface sediment characteristics found by Waddington and

Wright suggest a pattern similar to those summarized in Table 6, with higher values in the deeper holes. The values reported by Wildung and Schmidt (1973) are lower; their highest value was 0.17% and they observed only a slight correlation with depth. The EEDH core (Bradbury and Waddington 1973) showed sediments relatively rich in P (0.3–0.5%) in the upper 14 cm, reaching levels consistent with the deep-hole composite samples (Table 6) and the surface sediment analyses of Waddington and Wright (0.25–0.54%).

TP in Shagawa Lake sediments deposited before mining and logging activities began in the watershed (≈0.1%) is significantly lower than that in sediments deposited later. This difference is especially evident when the TP content of these precultural sediments is compared with that of the surficial sediments collected at lake depths >10 m (0.46%: Table 6).

The reserve of P from which release occurs each summer can be calculated from the phosphorus content of the sediments. The interstitial dissolved P in Shagawa sediments was generally 1–3 $mg \cdot liter^{-1}$ but as high as 4 in the top 10 cm in August 1976 (D.W.S. unpubl.). This suggests a reservoir of about 1,500 kg of dissolved P in the top 10 cm of the profundal zone and deeper water sediments (assuming 90% sediment water content and 3 $mg \cdot liter^{-1}$ interstitial P). If this reservoir were unreplenished, it would be easily depleted during the June–August summer pulse.

A better estimate of the releasable P reserve in the sediments comes from a calculation of the amount of NaOH-P present in the top 10 cm. Williams et al. (1971*b*) showed that this P fraction is readily exchanged with a dissolved P pool and thus is potentially mobile. We therefore estimated the size of this pool for the sediments at depths >6 m. Because the NaOH-P fraction was significantly higher for the deeper than for the shallower sites, the calculation requires area weighting. Our NaOH-P measurements left a gap between 7.5 and 10.5 m, so we estimated NaOH-P from the TP-NaOH-P relationship. First we determined the average TP for 1.5-m depth increments, then calculated the NaOH-P content and multiplied it by the volume of sediments for that 1.5-m increment. We used a water content of 90% and 10 cm as an estimate of the sediment mixed depth on the basis of core profiles of ^{106}Ru (W. C. Weimer pers. comm.). The calculations are summarized in Table 7. These results suggest a reservoir of nearly 50×10^3 kg of potentially mobile P in the profundal zone and deep-hole sediments, about 20 times the magnitude of the summer release.

Table 7. Estimate of NaOH-P reservoir in profundal zone and deep-hole sediments.

Depth increment (m)	Avg. TP (% dry wt)	NaOH-P (% dry wt)	Sediment vol ($m^3 \times 10^6$)	NaOH-P (kg)
6–7.5	0.187	0.064	2.47	16,300
7.5–9	0.197	0.074	1.75	13,600
9–10.5	0.278	0.155	0.60	9,800
>10.5	0.458	0.335	0.26	9,000

The impact of these internal phosphorus supplies and the implications for Shagawa Lake's recovery have been documented in the years following tertiary wastewater treatment. Although external P supplies are dramatically reduced and enough time has elapsed for complete recovery (Larsen and Mercier 1976*b*; Larsen et al. 1979), the lake continues to be highly productive, especially during July and August. At present it is not possible to predict with any degree of confidence how long internal P supplies will continue to regulate the productivity of the lake. Our work suggests that to restore productive lakes such as Shagawa within acceptable time limits, other measures will be needed in addition to external phosphorus curtailment.

References

AHLGREN, I. 1977. Role of sediments in the process of recovery of a eutrophicated lake, p. 372–377. *In* H. L. Golterman [ed.], Interactions between sediments and fresh water. Junk.

AMERICAN PUBLIC HEALTH ASSOCIATION. 1965.

Standard methods for the examination of water and wastewater, 12th ed.

BANNERMAN, R. T., D. E. ARMSTRONG, G. C. HOLDREN, AND R. F. HARRIS. 1974. Phosphorus mobility in Lake Ontario Sediments. Proc. 17th Conf. Great Lakes Res. 1974, p. 158–178.

BARICA, J. 1974. Some observations on internal recycling, regeneration and oscillation of dissolved nitrogen and phosphorus in shallow self-contained lakes. Arch. Hydrobiol. **73:** 334–360.

BRADBURY, J. P., AND J. C. WADDINGTON. 1973. The impact of European settlement on Shagawa Lake, northeastern Minnesota, USA, p. 289–307. *In* H. J. Birks and R. G. West [eds.], Quaternary plant ecology. Blackwell.

BURNS, N. M., AND C. ROSS. 1972. Oxygen-nutrient relationships within the central basin of Lake Erie, p. 85–119. *In* N. M. Burns and C. Ross [eds.], Project Hypo—An intensive study of the Lake Erie central basin hypolimnion and related surface water phenomena. CCIW Pap. 6, and U.S. EPA Tech. Rep. TS-05-71-2808-24.

CHAPRA, S. C. 1975. Comment on "An empirical method of estimating the retention of phosphorus in lakes" by W. B. Kirchner and P. J. Dillon. Water Resour. Res. **11:** 1033–1034.

COOKE, G. D., M. R. MCCOMAS, D. W. WALLER, AND R. H. KENNEDY. 1977. The occurrence of internal phosphorus loading in two small, eutrophic, glacial lakes in northeastern Ohio. Hydrobiologia **56:** 29–35.

FOREE, E. G., W. J. JEWELL, AND P. L. MCCARTY. 1971. The extent of nitrogen and phosphorus regeneration from decomposing algae. Adv. Water Pollut. Res., 1970, v. 2. Pap. 3-27, p. 1–15. Pergamon.

GALLEP, G. W., J. F. KITCHELL, AND S. M. BARTELL. 1978. Phosphorus release from lake sediments as affected by chironomids. Int. Ver. Theor. Angew. Limnol. Verh. **20:** 458–465.

GOLTERMAN, H. L. 1973. Natural phosphate sources in relation to phosphate budgets: A contribution to the understanding of eutrophication. Water Res. **7:** 3–17.

HOLDREN, G. C., JR., AND D. E. ARMSTRONG. 1980. Factors affecting phosphorus release from intact lake sediment cores. Environ. Sci. Technol. **14:** 79–87.

IMBODEN, D. M., AND S. EMERSON. 1978. Natural radon and phosphorus as limnologic tracers: Horizontal and vertical eddy diffusion in Greifensee. Limnol. Oceanogr. **23:** 77–90.

KAMP-NIELSEN, L. 1974. Mud–water exchange of phosphate and other ions in undisturbed sediment cores and factors affecting the exchange rates. Arch. Hydrobiol. **73:** 218–237.

———. 1975*a*. A kinetic approach to the aerobic sediment–water exchange of phosphorus in Lake Esrom. Ecol. Model. **1:** 153–160.

———. 1975*b*. Seasonal variation in sediment–water exchange of nutrient ions in Lake Esrom. Int. Ver. Theor. Angew. Limnol. Verh. **19:** 1057–1065.

KIRCHNER, W. B., AND P. J. DILLON. 1975. An empirical method of estimating the retention of phosphorus in lakes. Water Resour. Res. **11:** 182–183.

LAMARRA, V. A. 1975. Digestive activities of carp as a major contributor to the nutrient loading of lakes. Int. Ver. Theor. Angew. Limnol. Verh. **19:** 2461–2468.

LARSEN, D. P., AND K. W. MALUEG. 1976. Limnology of Shagawa Lake, Minnesota, prior to reduction of phosphorus loading. Hydrobiologia **50:** 177–189.

———, ———, D. W. SCHULTS, AND R. M. BRICE. 1975. Response of eutrophic Shagawa Lake, Minnesota, U.S.A., to point source phosphorus reduction. Int. Ver. Theor. Angew. Limnol. Verh. **19:** 884–892.

———, AND H. T. MERCIER. 1976*a*. Phosphorus retention capacity of lakes. J. Fish. Res. Bd. Can. **33:** 1742–1750.

———, AND ———. 1976*b*. Shagawa Lake recovery characteristics as depicted by predictive modeling, p. 114–137. *In* Water quality criteria research of the U.S. Environmental Protection Agency. U.S. EPA. Ecol. Res. Ser. Rep. EPA-600/3-76-079. Corvallis, Oregon.

———, J. VAN SICKLE, K. W. MALUEG, AND P. D. SMITH. 1979. The effects of wastewater phosphorus removal on Shagawa Lake, Minnesota: Phosphorus supplies, lake phosphorus and chlorophyll *a*. Water Res. **13:** 1259–1272.

LEE, G. F., W. C. SONZOGNI, AND R. D. SPEAR. 1977. Significance of oxic vs. anoxic conditions for Lake Mendota sediment phosphorus release, p. 294–306. *In* H. L. Golterman [ed.], Interactions between sediments and fresh water. Junk.

LIE, G. B. 1978. Phosphorus cycling by freshwater macrophytes—the case of Shagawa Lake. Ph.D. thesis, Univ. Minnesota.

MALUEG, K. W., D. P. LARSEN, D. W. SCHULTS, AND H. T. MERCIER. 1975. A six-year water, phosphorus, and nitrogen budget for Shagawa Lake, Minnesota. J. Environ. Qual. **4:** 236–242.

MEGARD, R. O., AND P. D. SMITH. 1974. Mechanisms that regulate growth rates of phytoplankton in Shagawa Lake, Minnesota. Limnol. Oceanogr. **19:** 279–296.

MORTIMER, C. H. 1941–1942. The exchange of dissolved substances between mud and water in lakes. 1 and 2. 3 and 4. J. Ecol. **29:** 280–329; **30:** 147–201.

———. 1971. Chemical exchanges between sediments and water in the Great Lakes—speculations on probable regulatory mechanisms. Limnol. Oceanogr. **16:** 387–404.

PORCELLA, D. B., J. S. KUMAGAI, AND E. J. MIDDLEBROOKS. 1970. Biological effects on sediment–water nutrient exchange. J. Sanit. Eng. Div., Proc. Am. Soc. Civ. Eng. **96:** 911–926.

RIGLER, F. H. 1973. A dynamic view of the phosphorus cycle in lakes, p. 539–572. *In* E. J. Griffith et al. [eds.], Environmental phosphorus handbook. Wiley.

SCHINDLER, D. W., AND OTHERS. 1973. Eutrophication of lake 227 by addition of phosphate and

nitrate: The second, third, and fourth years of enrichment, 1970, 1971, 1972. J. Fish. Res. Bd. Can. **30:** 1415–1440.

———, AND D. R. LEAN. 1974. Biological and chemical mechanisms in eutrophication of freshwater lakes. Ann. N.Y. Acad. Sci. **250:** 129–135.

SCHULTS, D. W., K. W. MALUEG, AND P. D. SMITH. 1976. Limnological comparison of culturally eutrophic Shagawa Lake and adjacent oligotrophic Burntside Lake, Minnesota. Am. Midl. Nat. **96:** 160–178.

SHEEHY, J. W., AND F. L. EVANS III. 1976. Tertiary treatment for phosphorus removal at Ely, Minnesota AWT Plant. U.S. EPA. Technol. Ser. Rep. EPA-600/2-76-082. Cincinnati, Ohio. 123 p.

SNODGRASS, W. J., AND C. R. O'MELIA. 1975. A predictive model for phosphorus in lakes. Environ. Sci. Technol. **9:** 937–945.

SONZOGNI, W. C. 1974. Effect of nutrient input reduction on the eutrophication of the Madison lakes. Ph.D. thesis, Univ. Wisconsin, Madison.

———, D. P. LARSEN, K. W. MALUEG, AND M. D. SCHULDT. 1977. Use of large submerged chambers to measure sediment-water interactions. Water Res. **11:** 461–464.

———, P. C. UTTORMARK, AND G. F. LEE. 1976. A phosphorus residence time model: Theory and application. Water Res. **10:** 429–435.

STAUFFER, R. E., AND G. F. LEE. 1973. The role of thermocline migration in regulating algal blooms, p. 73–82. *In* E. J. Middlebrooks et al. [eds.], Modeling the eutrophication process. Ann Arbor Sci.

SYERS, J. K., R. F. HARRIS, AND D. E. ARMSTRONG. 1973. Phosphate chemistry in lake sediments. J. Environ. Qual. **2:** 1–14.

TREUNERT, E., A. WILHELMS, AND H. BERNHARDT. 1974. Einfluß der Probenentnahme-Häufigkeit auf die Ermittlung der Jahres-Phosphor-Frachtwerte mittlerer Bäche. Hydrochem. Hydrogeol. Mitt. **1:** 175–198.

U.S. ENVIRONMENTAL PROTECTION AGENCY. 1971. Methods for chemical analysis of water and wastes. Anal. Qual. Control Lab. Cincinnati, Ohio. 874 p.

VOLLENWEIDER, R. A. 1968. Water management research. OECD Paris. DAS/CSI/68.27.

———. 1976*a*. Advances in defining critical loading levels for phosphorus in lake eutrophication. Mem. Ist. Ital. Idrobiol. **33:** 53–83.

———. 1976*b*. Rotsee, a source, not a sink for phosphorus? A comment to and a plea for nutrient balance studies. Schweiz. J. Hydrol. **38:** 29–34.

WELCH, E. G. 1977. Nutrient diversion: Resulting lake trophic state and phosphorus dynamics. U.S. EPA. Ecol. Res. Ser. Rep. EPA-600/3-77-003. Corvallis, Oregon. 100 p.

WILDUNG, R. E., AND R. L. SCHMIDT. 1973. Phosphorus release from lake sediments. U.S. EPA. Ecol. Res. Ser. Rep. EPA-R3-73-024. Corvallis, Oregon. 185 p.

WILLIAMS, J. D., J. K. SYERS, D. E. ARMSTRONG, AND R. H. HARRIS. 1971*a*. Characterization of inorganic phosphate in noncalcareous lake sediments. Soil Sci. Soc. Am. Proc. **35:** 556–561.

———, ———, R. F. HARRIS, AND D. E. ARMSTRONG. 1971*b*. Fractionation of inorganic phosphate in calcareous lake sediments. Soil Sci. Soc. Am. Proc. **35:** 250–255.

Submitted: 21 October 1977
Accepted: 18 December 1980

NOTICE

This document has been reviewed in accordance with U.S. Environmental Protection Agency policy and approved for publication. Mention of trade names or commercial products does not constitute endorsement or recommendation for use.

This article documents research that was conducted under the auspices of the U.S. Environmental Protection Agency (USEPA). As an arm of the government, the USEPA has a paid up, non-exclusive, irrevocable, worldwide license to reproduce, prepare derivative works, and distribute to the public all of the material contained herein, and to grant others acting on its behalf the right to do so. The USEPA grants to the National Technical Information Service, Department of Commerce, the right to act as its agent in the distribution of this material.